

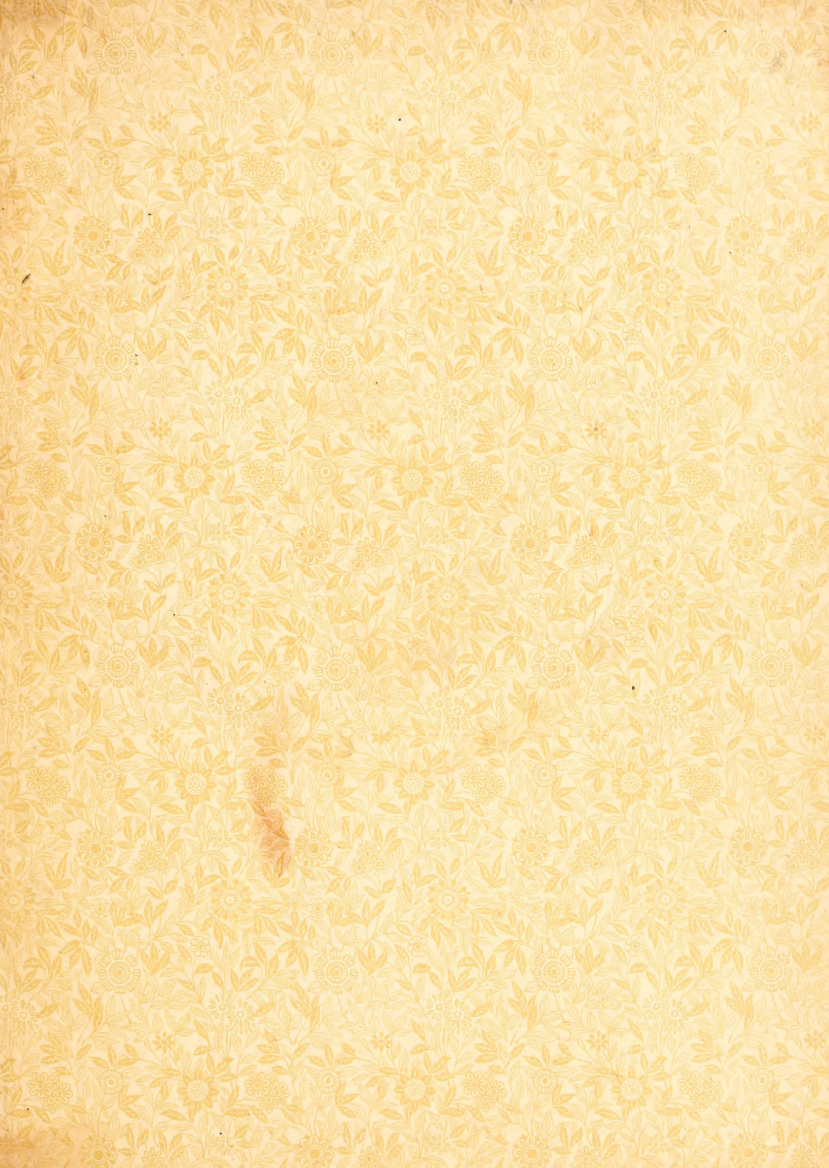
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THE
DOUBLE HALIDES OF ANTIMONY
WITH
ANILINE AND THE TOLUIDINES
DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY
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INTRODUCTION.

There has been known for a long time a large number of substances which it has been impossible to harmonize with regular chemical compounds according to the recognized rules of balance.

These substances have received various names which were intended to explain their character, but as long as the nature of the substances was not well understood, a course any number of names would not accomplish the desired end. As examples of these names may be mentioned that of Molecular Compounds, Addition Products and Double-Salts.

In account of the obscure nature of these substances they are generally entirely ignored, or given merely a passing

notice in the text-books.

A few years ago Professor Klemm reviewed the literature of the subject and presented in a concise article all that is known regarding the matter and has supplemented this knowledge by the statement of a law which seems to underlie the formation of all double halides.

Before stating this law and discussing the facts which led to its deduction it may not be out of place in this connection to give a brief résumé of some of the views that have been held upon the subject of the double halides.

In general, a double halide compound consists of the chemical union of the halide of a basic element, or group of elements having basic properties with

The corresponding halide of some more
active element, for example, potassium
chloride with nitric acid, to
form potassium chloronitrate,
 $\text{KCl} \cdot \text{SbCl}_3$; or again, adding hydrochloric
acid with nitric acid to form
nitric chloronitrate,
 $\text{Cl}_2 \cdot \text{H}_2\text{O} \cdot \text{HCl} \cdot \text{SbCl}_3$.

It is a rather remarkable
fact that the number of double halides
which exist only of univalent elements
is very small. Many of the bivalent
elements, such as those arranged in
Group II. of the Periodic System, form
two series of double halides with univalent
metals of the first group, for example
 $\text{HgCl}_2 \cdot \text{KCl}$ and $\text{HgCl}_2 \cdot 2\text{KCl}$.

The halogen salts of the
bivalent elements, such as bromides.

antimony and chromium form in a similar way three classes of compounds.

Leaving out of account all double cyanides salts whose formation seems to depend upon some law peculiar to nitrogen, it has been observed that almost without exception there is a certain regularity to which all other double-halides conform.

Related in the words of Professor Rosen the law is as follows:-

"When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter."

At the time the article referred to was written it was stated that out of over four hundred double halides there was but one which did not seem to conform to the above law. This compound has the composition $\text{CaCl}_2 \cdot 2\text{KCl}$. By an extension of the theory which was framed to explain the constitution of other double halides this compound has been satisfactorily accounted for. The discussion of this will be taken up a little later.

In examination of certain oxygen compounds formed by the substitution of metallic hydrides in the hydrides of the alkali metals a striking analogy to the double halides is seen, both as respects the mode of formation and the composition. As examples of the above mentioned oxygen compounds the following may be

$\text{H}^+ - \text{OH}^-$ $\text{H}^+ - \text{OH}^-$ $\text{H}^+ - \text{O}^-$
 $\text{H}^+ - \text{O}^-$ $\text{H}^+ - \text{O}^-$ $\text{H}^+ - \text{O}^-$
 and $\text{H}^+ - \text{O}^-$

Compared with the alkaline hydroxides the other hydroxides are acidic; so in the double-halides there is union between a relatively acidic halide salt with a relatively basic halide salt. Furthermore, the analogy with composition of these oxygen compounds with the double halides is seen by an inspection of formulas of both classes of compounds; for example, $\text{K}_2\text{O}_2\text{Cl}_2$ and $\text{K}_2\text{O}_2\text{Cl}_2$ in which two oxygen atoms are equivalent to four chlorine atoms, or rather play an analogous role. v. Bunsen¹ and Boullay² independently of each other were the first to point out this distinction between acidic and basic halides. This view was objected to by Liebig³ and later by Berzelius⁴ on the ground that if a substance was a salt of

1. Ann. Chem. Phys., xxxiv, 142
 2. Ibid. xxi, 437.

3. Ibid. xxxv, 68
 4. Jahrb. 3, 156

could possess neither acidic nor basic properties.

This objection had great influence on the non-acceptance by chemists of the view of v. Dorff and Tschuganoff, and little was heard of their theory until about the year 1840, when Dr. Wenz of Philadelphia offered the following definition of salts.

"When two compounds capable of combining with each other to form a certain product have an ingredient common to both, and one of the compounds presents the positive and the other the negative pole of the voltaic series we must declare the former an acid, the latter a base."

Granting the analogy in composition and mode of formation to exist between the zepher salts and the double-halides, the structure of the latter finds easy explanation. 'Vaquet' expresses himself in this

point in 1867 in his "Principes de Chimie" by suggesting that two halogen atoms acting together can play the same part that the so-called linking oxygen atom plays in many cases. He gives the formula $\text{X} \cdot \text{X} \cdot \text{C} \cdot \text{X}$ to illustrate his idea.

Views of a similar nature have been advanced by 'Bernstrand' in 1889, by 'Jørgensen' in 1897, by 'Mallet' in 1851 and by others. Certain objections to the theory that two halogen atoms may play the rôle of the linking oxygen atom have been urged. Among the foremost of these is that of 'Korotmann', which appeared in his "Theoretische Chemie", p. 340. It is simply that the view is not in accordance with the prevailing ideas regarding the valence of the halogens. In the present condition of the knowledge respecting valence the objection is

not a very forcible one.

More recently other objections have been brought forward, but they will not be taken up in this place.

Recent researches in the field of double salts have brought to light the existence of certain compounds of this order which do not find satisfactory explanation by means of the views thus far held, making it necessary therefore to somewhat extend the theory.

There are, for example, the two salts CuCl_2 and $\text{ZnCl}_2 \cdot 4\text{HCl}$. The former salt discovered by Mitscherlich¹ has been re-investigated and found to exist. The second salt, found by v. Hauer², has also been re-examined and it is believed, has the formula assigned to it. There have since been found other compounds of this character which cannot be explained by the hypothesis of the double

1. Ann. Chem. Phys. 1829, 10.

2. Ber. Ges. Chem. 1851, 10.

halogen atoms acting as a trivalent group.

Three such compounds have been brought to light in the course of the present investigation.

The compounds referred to are as follows:-

Tetraiodine bromo-antimonite represented by the formula $(C_6H_5.NH_2.HI)_4.Sb.Br_3.I_3.O_2$

delta-p. Iodine bromo-antimonite $(C_6H_5.CH_3.NH_2.HI)_4.Sb.Br_3$ and

tetraiodine iodo-antimonite

$(C_6H_5.NH_2.HI)_4.Sb.I_3$.

In all such exceptional cases Professor Preman suggests that it may be necessary to assume that three halogen atoms acting together form a trivalent group $-(Cl)_3-$ or, assuming that chlorine is trivalent, the group must be represented structurally thus:- $-Cl \begin{smallmatrix} Cl \\ | \\ Cl \end{smallmatrix} -$

METHODS OF ANALYSIS.

Antimony and the halogens only were estimated in each salt.

Determination of Antimony.

About 0.3 gram of the dried salt was weighed off into a 100 cc beaker and after dissolving in a few cubic centimeters strong solution of tartaric acid, the whole was considerably diluted with water and then heated to boiling. The solution was then acidified with metaphosphoric acid and a stream of hydrogen sulphide passed into the solution for some time. When the antimony had been completely precipitated as the sulphide, Sb_2S_3 , the liquid was heated for some time to drive off the hydrogen-sulphide. The precipitate was then collected on a porcelain dish filter and washed successively with water, alcohol,

Other and carbon bisulphide; the alcohol and ether rendered the precipitate free from water, while the carbon bisulphide removed the free sulphur.

The crucible with its precipitate was next placed in a hot-air bath which was kept filled with carbon dioxide while the bath was slowly heated up to about 250°C . and kept at this temperature for one hour. At the end of that time the bath was cooled down to the normal temperature, but the current of carbon dioxide was kept going till the bath was cool.

The crucible and precipitate were weighed and the antimony sulphide, Sb_2S_3 , calculated to metallic antimony.

Determination of Halogens.

The usual gravimetric method was employed for each of the Halogens, Chlorine, Bromine and Iodine, and requires no special comment here.

The atomic weight values employed in the calculation of the results are as follows:-

Silver	108		
Chlorine	35.5	Bromine	80
Antimony	120	Carbon	12
Sulphur	32	Nitrogen	14
Iodine	127	Hydrogen	1

Description of Experiments.

The ground object the following experiments is intended to cover included a study of the compounds formed by the halogen acid derivatives of salicylic acid and the tellurides with the corresponding halides of antimony.

The method of preparing the salts was to bring the halide of the base together with the corresponding halide of antimony, each constituent being previously dissolved in the corresponding halogen acid. The results were found to be most satisfactory when each solution was heated before mixing, the base was then added to the metallic chloride.

The plan adopted in making the analyses was to add the halide of the metal in gradually increasing quantities.

proportion to one molecule of the halide of the base. Since in no case the analysis of any of these mixtures indicates that more than one molecule of the halide of the metal had combined with one molecule of the halide of the base mixtures were not made containing more than three molecules of the halide of the metal to one molecule of the halide of the base. Similar trials were then made in the other direction; i.e., one molecule of the metallic halide was mixed with a gradually increasing number of molecules of the halide of the organic base in the ratio of one to two, one to three, one to four and one to six respectively.

The limit of double salt formation in this direction was considered reached, since in many cases the halide of the base crystallized out even in mixtures of one to three

and in no case was a salt formed which contained more than four molecules of the halide of the base to one of the anion.

Every mixture made produced a soluble salt of some kind. When the solutions were of the proper consistency the formation of the crystals was of a uniform character, and they were easily obtained, as usual, in that condition. The compounds formed differed markedly in their powers of crystallization, but as the formation of crystals with well-defined angles and faces would require days and often weeks, no special attempt was made to produce and study the substances crystallographically. Such investigation was further interfered with by the fact that many of the substances rapidly underwent changes which rendered them unfit for that study.

A few notes, however, of a crystallographic character kindly furnished by Mr. F. C. Spencer of the Geological Department of this University, will give an idea of the nature of some of the substances in this respect.

As a rule if the first crops of crystals were found to be uniform in appearance they were subjected to chemical analysis, the determination of the halogen and the solubility being considered sufficient for the identification of the substance. The results of the analysis of the compound formed from each mixture are placed in a table at the end of the description of these compounds.

Under each mixture is placed the results of the analysis of the compound obtained from that mixture, and in a

smaller table is found the summary of the results of the analyses grouped under the formulas of those compounds which the analyses seem to indicate have been formed.

Experiments with Antimony Hydrochloride and Antimony Trichloride

The results of the experiments with antimony hydrochloride and antimony trichloride will now be taken up in detail.

From mixture No. 1, one part (molecule) of the base chloride to one of the metallic chloride, there crystallized out a colorless salt in thick irregular prisms, which on analysis, gave results for chlorine and antimony as recorded in column one of Table I. In comparing these results with the theoretical values which would be obtained

if a compound, called for by the one at the head of column six, had been formed no agreement between their values was found, but as these experimental results did compare with the theoretical percents. of the compound heading column five, it was concluded that a compound was formed having the composition expressed by the formula $(C_6H_5)_3N \cdot NCl_3 \cdot SbCl_5 \cdot H_2O$ and which may be called trianiline chloroantimonate.

Properties of the Compound

This substance crystallized in thick, colorless hexagonal prisms having the appearance shown in the accompanying figure. The action of a number of solvents was tried upon the substance and it was found to dissolve quite easily even in all the above



mineral acids, as well as in a mixture of the organic acids in concentrated form, e.g. tartaric and acetic acids. It required rather strong stage and methyl alcohol to effect solution. Water, or dilute alcohol, precipitated a white antimony compound. On boiling a solution of the salt the odor of nitro-benzol was given off. On slightly heating the dry substance in an open tube it was rapidly decomposed, hydrochloric acid being given off.

After exposure to the air for several days, the substance acquired an opaque greenish appearance. On heating specimens several months no further change in appearance seemed to occur.

The results of an analysis of mixture N^o 2 in which the constituents were combined in the proportion of one

molecule of antimony trichloride to two molecules of antimony trichloride, pointed to a compound of the formula — $C_6H_5.NH_2.HCl.3PCl_2.H_2O$. Monaniline — chlorantimonite crystallized out in long, thin colorless plates. In general, its properties were found to be similar to the first salt described. Discrepancies in the antimony analyses were probably due to the presence of water and sulphur in the antimony trisulphide precipitate. In the later analyses this difficulty was overcome by washing the precipitate with alcohol, ether and carbon disulphide.

Analyses of mixture No. 3 showed that monaniline chlorantimonite was again formed. Mixtures four, five and seven, each in turn produced one and the same compound; viz. trianiline

intermediate the compound has appeared
above.

The results recorded include the
analyses of both first and second
crops of crystals, but in no case did
second crop give any difference.

TABLE I.

Double Salts of Uniaxially Trichloride and Diammonium Trichloride

	I	II	III	IV	V	VI	VII
	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3$	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$	$C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$
SB	33.70	31.02	41.22	37.36	44.41	43.73	38.22
CL	19.77	17.77	36.46	41.11	43.71	43.71	35.11
SB	19.18	34.11	32.71	19.01			
CL	33.51	37.36	37.54		33.54		
SB	19.53	33.90	32.62	19.50	19.18		
CL	33.69	37.46	38.08	33.63	33.50		
SB	19.74	34.68	32.66	19.28	19.10		
CL	33.23	37.77	38.13	33.77	33.24		
SB		33.51			19.09		
CL		37.38			33.27		
SB							
CL							

SUMMARY I.

1. $C_6H_5 \cdot NH_2 \cdot HCl, SbCl_3 \cdot H_2O$ ($C_6H_5 \cdot NH_2 \cdot HCl$)_{1/2} $SbCl_3 \cdot H_2O$ 1

	SB	CL	SB	CL
Theor.	32.08	37.97	19.98	33.67
Experimental	32.62	38.08	19.08	33.54
	32.71	38.13	19.18	33.50
	32.66	37.54	19.10	33.24
	33.51	37.36	19.08	33.29
	33.90	37.47	19.01	
	37.38		19.50	33.63
	37.46		19.28	33.77
			19.18	33.31
			19.74	33.27
			33.27	
			33.27	

Experiments with *o*-Toluidine Hydrochloride and
Antimony-Trichloride.

Experiments were next undertaken in the
o-toluidine series, this line of work being car-
ried out in a manner similar to that
followed in the experiments with aniline.

The analyses of the compounds resulting
from the several mixtures in this series
point to the existence of only one compound,
viz, diortho-toluidine-chlor-antimonite,
having the composition expressed by the formu-
la $(C_6H_4, CH_3, NH_2, HCl)_{1/2} \cdot SbCl_3$.

A large quantity of colorless crystals
separated out from mixture No 5 which,
when dissolved and tested with hydrogen-
sulfide, gave no antimony reaction.

The substance was therefore the halide of
the base, the removal of the mother liquor
from these crystals, a compound of 2

different form at once separated out, which proved to be the double salt above mentioned.

This substance, as usually formed, did not differ much in appearance from the aniline salts already described. It was allowed to form to justify the tendency of both the aniline and all the toluidine chlor-antimony salts is to crystallize out in beautiful sheaf-like masses with a satin lustre.

The analytical results of the study of this series are placed in Table II under the Summary which follows.

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Double Salts of Ortho-Toluidine Hydrochloride with Benzylamine

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SUMMARY



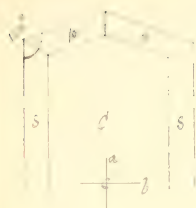
86	CL
11	14
28.6	10.4
1.1	34.44
27.9	34.48
28.6	34.56
	34.74
	34.87
	34.89
	34.91
	34.92

Experiments with m-Toluidine Hydrochloride and
Antimonytrichloride

As in the case of the o-toluidine experiments the hydrochloride of the m-base was mixed in various proportions with the chloride of antimony. On examination of the compounds obtained from each of the seven mixtures made only two substances were found which proved to be different from each other. Each of the seven mixtures, except the third, gave a compound having the formula, $(C_7H_7Cl)_2Sb_2Cl_3$, which should be named m-Toluidine

chloroantimonate. This substance always crystallized in thin orthorhombic tablets in the form of radiating groups, and perfectly transparent and colorless.

Following is a brief crystallographic account of one of the crystals I examined.



Orthorhombic System

c = basal plane

p = brachypinacoids

S = macrodomes

a = a

Mixture H² S gave a compound, which an analysis pointed to a substance whose composition should be expressed by the formula $(C_6H_4Cl_2 \cdot NH_2 \cdot COCl)_2 \cdot 5SOCl_2 \cdot H_2O$.

An analysis of one sample of the substance pointed to the previous substance, without data of crystallization.

The only form in which this compound was obtained was in fine granular crystals.

The results of experiments with N-bromine compounds are recorded in Table III. and Summary III.

Double Salts of *m*-Toluidine Hydrochloride

	I	II	III	IV	V	VI	
	$C_2H_4, NH_2, NH_2, HCl, SbCl_5, H_2O$	$C_2H_4, NH_3, NH_3, HCl, SbCl_5, H_2O$	$C_2H_4, NH_3, NH_3, HCl, SbCl_5, H_2O$	$C_2H_4, NH_3, NH_3, HCl, SbCl_5, H_2O$	$C_2H_4, NH_3, NH_3, HCl, SbCl_5, H_2O$	$C_2H_4, NH_3, NH_3, HCl, SbCl_5, H_2O$	
SB	32,43	40,13		23,30	22,57	18,26	SB
CL	38,38			34,56	33,35	32,42	CL
SB	19,87	19,87	22,05	19,87	19,87	19,87	SB
CL	31,51	31,58	33,14	32,14	32,35	32,25	CL
SB	19,73	19,86	22,78	19,73	19,73	19,73	SB
CL	32,41	32,43	33,28	32,19	32,09	32,29	CL
SB			23,11				SB
CL			34,05				CL

SUMMARY

Theor.	Sb	Cc
	18,26	32,42
	18,61	32,29
	18,65	32,38
	18,82	32,25
	18,79	32,69
	18,76	32,35
	18,78	32,37
	18,03	32,01
	18,20	32,28
	18,17	32,03
	18,11	32,01
	18,11	32,01
	18,11	32,01

Experiments with *p*-Toluidine Hydrochloride and its Salts
To be made

In carrying out the same general method of experiment with this series of compounds the analyses of the substances formed from the various mixtures pointed to the formation of only two different bodies, viz, di-*p*-toluidine chloroantimonite, having the formula, $(C_6H_4 \cdot CH_3 \cdot NH_2 \cdot HCl)_2 \cdot SbCl_3 \cdot H_2O$, and tri-*p*-toluidine chloroantimonite, $(C_6H_4 \cdot CH_3 \cdot NH_2 \cdot HCl)_3 \cdot SbCl_3 \cdot H_2O$.

Mixtures one, two, three and four produced the second of the above compounds while the first was formed only by mixture five.

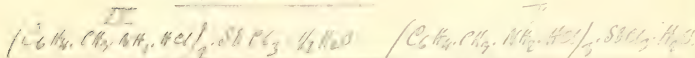
The tri-compound forms in colorless granular crystals while the di-compound came in long, colorless silky needles. Neither of these compounds seem to undergo any change on being kept for months. The analytical results are recorded in the following table.

TABLE

Double Salts of 70 Toluidine "Gärchelecke" and Bromine

	I	II	III	IV	V	VI	VII	VIII
	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$	$(C_6H_4.CH_3.NH_2.HCl)_2$
SB	12.61	12.61		12.16	12.77	12.16	12.16	12.16
CL				14.10	14.93	14.10	14.10	14.10
SB	13.65	13.40	12.68	12.09	13.27			13.27
CL	33.52	33.66	33.16	33.13	31.54			31.54
SB	13.58	13.50	12.03	12.61	18.21			18.21
CL	33.49	33.95	33.02	33.11	28.11			28.11
SB					18.27			18.27
CL	33.10				31.16			31.16
SB					18.11			18.11
CL					31.25			31.25

SUMMARY



	SB	CL
Theor.	12.97	33.85
	13.40	33.82
	13.58	33.49
	13.65	33.66
	13.50	33.38
	13.61	
	14.03	

	SB	CL
	12.77	31.55
	12.29	31.10
	12.61	31.55
	12.27	31.10
	12.11	

Experiments with Aniline Hydrobromide and Antimony-
Tribromide.

The following series of mixtures of the above substances were made in hydrobromic acid solution: one molecule of the former to one of the latter one to two, one to three, two to one, three to one, four to one and six to one. In beaker one there was formed a copious crop of fine light-yellow needles.

In No 2 there was a scant crop of two kinds of crystals one kind being thin, flat rectangular plates the other, yellow granular crystals. Mixture three gave yellow needles, similar in appearance to those in beaker 1.

In beaker 4 was formed a small crop of yellow needles along with larger yellow granular crystals. A copious crop of light-yellow scaly crystals were formed in beaker 5. In No 6 appeared a copious crop of

yellow granular crystals. A copious crop
of irregular flat, thick whitish yellow
plates formed in beaker 7.

As in each case the crystals had
formed too rapidly to be well-defined and
uniform, all the crops were redissolved,
the solutions somewhat diluted and again
set aside to crystallize out. The next
series of crystals were generally of better
form. Sifts from beakers 1, 2, 3, 4 and 5
crystallized out in centimeter-long, many-
yellow, lath-shaped crystals of the orthorhombic
system being of the form shown in the
accompanying figure.



The cleavage is parallel to a.

The crystals also showed parallel

extinction in polarized light.

A chemical analysis of each of
these five crops resulted in

pointing to only one chemical compound,
which is represented by the formula —
 $\text{Fe}_2\text{O}_3 \cdot \text{NH}_3 \cdot 4\text{H}_2\text{O}$, H_2O , and receives the name —
hemine brom-antimonide. It is of a
canary-yellow color and translucent, stable
in the air, undergoing no perceptible change
on being kept for several months. The analyses
showing its composition are given in the follow-
ing tables. Mixtures 3 and 4 produced
substances which range of the same yellow
color, differing markedly in their crystal
habit. This will best be indicated by figures.

Clearage is parallel to a and
perfect. Habit tabular and
perpendicular to a. System
orthorhombic. pr. faces slightly
developed on one side.

a = brachypinacoid, c = basal plane

pr = micropinacoids, m = macro-pinacoids.

37

An analysis of this salt showed it to have a rather unusual composition there being four molecules of the halide of the base combined with one molecule of the halide of the antimony. The composition is expressed by the formula $4\text{RbCl} \cdot \text{NH}_4 \cdot \text{HBr}_4 \cdot \text{SbBr}_3 \cdot 4\text{H}_2\text{O}$ and the compound receives the name Antimonite from antimonite. It was found impossible to determine the water of crystallization by exposure of the substance over sulphuric acid, since after a short treatment of this kind dense fumes of hydrobromic acid were given off on opening the desiccator.

On preserving crystals of the substance for some time in the air they gradually became opaque. The results of the above experiments are recorded in Table for

TABLE I

Double Salts of Aniline Hydrobromide and Potassium Picramate

	I	II	III	IV	V	VI	VII	VIII
	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$	$(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3 \cdot H_2O$
SB	22.47	24.5	18.71	16.48	16.5	17.60		SB
Br	53.9	54.64	53.73	56.49	55.10	54.46		Br
SB	4.74	17.45	16.53	16.77		16.40	11.20	SB
Br	50.78	57.05	56.01	56.59		56.39	52.26	Br
SB		11.55	10.34				11.24	SB
Br		54.10	55.12					Br
SB							11.07	SB
Br							52.62	Br

SUMMARY V

IV. $(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3$ VI. $(C_6H_5NH_2 \cdot HBr) \cdot SbBr_3$

Theoret.	SB	Br	SB	Br
	16.34	54.78	11.00	51.16
	17.45	57.05	11.14	51.77
	16.53	56.01	11.00	
	16.34	55.12		
	16.77	56.59		
	16.10	55.07		

Experiments with α -Toluidine Hydrobromide and Antimony Tribromide

The experiments were carried out in the usual manner with this series of substances.

Out of the seven various mixtures which were made, from the appearance of the crystals which were formed, only one kind of compound seemed to be produced.

The crystals of this substance had the same general appearance in each beaker, being of a light-yellow color. The crystalizing-force of the substance seemed to be weaker than that of any of the compounds previously found. Small, short, blunt prisms crystallized out both as first and second crops from the same beaker.

Determinations of bromine and antimony led to the conclusion that tri- α -toluidine brom-antimonide, $\text{R}_3\text{Br}_3\text{As}_2$ or $\text{R}_3\text{Br}_3\text{Sb}_2$.

is the only compound which can be formed from the reactants employed.

TABLE V

Double Salts of *c*-Toluidine Hydrobromide and Antimony Tribromide

	I	II	III	IV	V	VI	VII	VIII
Formula	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$	$C_8H_8, CH_2, NH_2, HBr, S_8Br_2$ $C_8H_8, CH_2, NH_2, HBr, S_8Br_2, H_2O$
Weight	11.84 11.20 50.59	16.41 15.91 51.70	17.79 17.99 51.07	18.70 17.81 51.05	16.74 16.74 51.71	16.74 16.74 50.36	16.74 16.74 51.56	16.74 16.74 51.56
SB	13.17	13.57	12.50	12.67	12.87	12.78	12.66	12.66
Br	50.63	51.70	50.62	50.76	51.71	51.26	51.56	51.56
S ₈	51.07		51.24	51.57				
Br	50.57							

SUMMARY II

V $(C_5H_4.C_6H_3.AH_6.HD_5)_3$. S. 6.

Theoret	86	Dr
12.71	51.98	
13.17	57.14	
13.37	1.70	
12.80	57.29	
12.07	51.7	
12.11	1.71	
12.78		
6.10		

Experiments with *m*-Toluidine Hydrobromide and Nalmony Trisulfonate

Experiments were made in this series with various mixtures of the two constituents.

Out of the seven combinations made, only one kind of compound was found on analysis. This substance crystallized out in each beaker in long, very pale-yellow, silky needles. The air-dried salt was more opaque and yellower than when observed in the mother liquor.

The analysis of the result of each mixture pointed to one compound only, and this should have the composition expressed by the formula $(C_7H_7.CHS.NH_2.HBr)_2.O_6Br_3$ and called *m*-toluidine trisulfonate.

The results of the analyses are tabulated as follows -

TABLE VII.

Doubled salts of m. blue green hydrochloride and fat

[illegible]

SUMMARY VII

IV. $(C_5H_8, CH_2, NH_2, HBr)_2$ SiH_4

Theret.	16	17
	16.71	54.49
	16.66	54.86
	16.47	54.76
	15.96	54.03
	15.89	53.77
	15.65	53.49
		53.40
		53.37
		53.31
		53.24

Experiments with p-toluidine hydrobromide and
dull-mary tolbenamide

The mixtures of the constituents were made in the usual way in hydrobromic acid solution. Mixtures one, two, four, five and seven all gave crops of silver-white needles. Repeated attempts were made to get a salt from mixture No 6, but it was possible only to obtain the p-toluidine hydrobromide from the solution.

Mixture No 3 gave a crop of very small lemon-yellow plates. Owing to the ease with which the white salts give up or take up water of crystallization it was difficult to get sharp analytical data.

The analyses of all the salts obtained seem to point to the existence of three different compounds, and one of them also with water of crystallization.

They are as follows:— Di-p-toluidine—
brom-antimonite, $(C_6H_4.CH_3.NH_2.Br)_2 SbBr_3$,
the same compound with one molecule of
water of crystallization, $(C_6H_4.CH_3.NH_2.Br)_2 SbBr_3.H_2O$,
Tri-p-toluidine-brom-antimonite,

$(C_6H_4.CH_3.NH_2.Br)_3 SbBr_3$, and tetra-p-tolu-
idine brom-antimonite, $(C_6H_4.CH_3.NH_2.Br)_4 SbBr_3$.

In dry air these compounds are
canary-yellow; but if exposed to the air
on a damp day they change over to snow-
white. The compound which crystallized
out from mixture three, in the form of
small plates, seems to be quite stable as
to its color - it remains yellow both in
moist and in dry air. The mixture

which crystallized from mixture one although
when analyzed pointed to the same compound
without water of crystallization, crystallized
in needles, so that the boiling up of

by the one substance and not by the other
may be dependent upon the crystalline
form. The yellow color can be restored
in all three compounds by gently heating
a portion on a piece of platinum foil.

The analyses of the compounds are
tabulated in the report under Analysis.
Note. On exposing the compounds, which an
analysis showed the presence of water of
crystallization, in the desiccator over concen-
trated sulphuric acid, there was a constant
loss of weight, i.e., presumably, to the
evolution of hydrochloric acid.

TABLE XL.

Double Salts of *p*-Toluidine Hydrobromides and Nitrobenzene

	I	II	III	IV	V	VI	VII
	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 2H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$
Cal.	16.39	16.90	16.43	16.41	16.41	16.41	16.41
Found	16.39	16.86	16.38	16.35	16.35	16.35	16.35
Cal.		16.04		16.05	16.05		
Found		16.04		16.05	16.05		
Cal.		16.79		16.79	16.79		
Found		16.79		16.79	16.79		
Cal.	53.31		53.31	53.31	53.31		53.31
Found	53.31		53.31	53.31	53.31		53.31
Cal.	51.15		51.15	51.15	51.15		51.15
Found	51.15		51.15	51.15	51.15		51.15

SUMMARY II

	IV	V	VI
	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$	$C_6H_4(CH_3)NH_2 \cdot HBr \cdot 16H_2O$
Cal.	16.39	16.41	16.41
Found	16.39	16.35	16.35
Cal.	16.04	16.05	16.05
Found	16.04	16.05	16.05
Cal.	16.79	16.79	16.79
Found	16.79	16.79	16.79
Cal.	53.31	53.31	53.31
Found	53.31	53.31	53.31
Cal.	51.15	51.15	51.15
Found	51.15	51.15	51.15

Experiments with the Iodide Series

Study with this series was begun with the aniline salt. More difficulty was experienced here, since it was necessary to prepare the hydriodic acid only in such quantities as would be immediately needed, owing to its rapid decomposition. It was also difficult to avoid the separation of free iodine when heating the mixture.

A convenient method for making hydriodic acid is to gradually add four grams dry yellow phosphorus, in small pieces, to 44 grams crystallized iodine, in a round bottom hard-glass flask.

When all the phosphorus has been added and the reaction product, phosphorus tri-iodide, is quite cool, six grams water is added to the white mass.

The flask is then connected to a receiver.

flask containing about 100 cubic centimeters of water. The first flask is very gently heated & driven over the hydriodic acid. The water in the second flask absorbs the acid without danger of the former being drawn back into the distilling flask, if the end of the connecting tube is about one centimeter above the surface of the water.

The mixture of the aniline and antimony halides were made up in the usual proportions hitherto employed.

A crop of finely divided granular scarlet crystals separated from mixture No. 1.

On drying in the air these seemed to undergo no kind of decomposition. A determination of antimony and iodine clearly pointed to the existence of a compound whose composition should be expressed by the formula $\text{C}_6\text{H}_5\text{NO}_2\text{SbI}_3$. Then water

iod. antimonide

Out of mixture two, small almost microscopic scaled octahedra, with modified edges crystallized out. An analysis of these revealed no new compound. Crystals from mixture three, again in the form of modified and tapered octahedra, proved on analysis to be identical with the first compound discovered in this series. Mixtures Nos. four and six yielded nothing new in the way of double-salts. Mixture five, on the other hand, yielded a beautiful crop of fine carmine-colored needles, which on analysis proved to be a combination not yet met with in the present investigation. The compound is composed of three molecules of aniline hydroiodide and two of antimony tri-iodide, expressed by the formula $(C_6H_5NH_2)_3I_3 \cdot 2SbI_3$.

The last mixture examined was that in which the ratio of the constituents was six to one. A new compound seemed to be formed here. The mixture from which the compound was finally obtained yielded at first only a large crop of the halide of the base. In evaporating the mother liquor, a crop of uniform golden-yellow plates was obtained. These were dried and heated for analysis. It was found to be present in considerable quantity. As soon as the crystals were drained off they began to undergo a change in color, from golden-yellow to orange-red.

When dry they were analyzed and gave results pointing to the formula $C_{12}H_{10}O_2$ in agreement with the structure.

The analytical results of the study of this series are gathered together in Table II.

TABLE II

Double Salts of Aniline Hydrochloride and Aromatic Triamines

	I		II		III		IV		V		VI		VII		VIII	
	$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$		$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$	
16	16,62	16,61	16,62													
17	70,10	70,64	70,65		70,05		70,34		70,05		70,29		70,29		70,29	
18	14,78			70,31	70,14		70,14		14,56							
19	70,11								70,11							
20	16,80								14,75							
21	70,44			70,37	70,10		70,25		70,25		70,29		70,29		70,29	

SUMMARY

$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$

$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$

$(C_6H_5NH_2 \cdot HCl) \cdot 3H_2O$

Wt. per cent	56	7	14	56	9	14	56	9	14
	14,02	9,30		14,41	68,64		8,66		
	16,78	70,18		14,2	68,64		8,24		
	16,80	70,44		14,48	68,31		8,24	68,31	
		70,31		14,14	68,35				
		70,39		14,44	68,35				
		70,14							
		70,10							
		70,84							
		70,06							

Experiments with α -Toluidine Nitrosodichloride Nitrosomethyl-dichloride

The usual experiments were made with the above ingredients and no difficulty was experienced in obtaining well-characterized products in the case of each experiment.

The subb-salts which crystallized out from each of the first three mixtures had the same general appearance, consisting of short blunt needles of a brick-red color.

Analyses of the three sets of crystals pointed to one and the same compound, containing one atom of each of the original ingredients. The formula expressing the composition may be shown by the following formula:
 $C_6H_4Cl_2NH_2 \cdot HCl \cdot SO_2Cl_2$, non- α -toluidine nitrosodichloride
An examination of the subb-salts formed from mixtures four, five, six and seven indicated that a new series of

been formed. The appearance of the crystals
in the above cases was quite different from
that of the first component described. They
consisted of irregular-shaped bronze-colored
leaves. (Analysis of a sample of each not
indicated that only one individual had been
formed, viz; As_2O_3 to which As_2S_3 was added.
(As_2S_3 100, As_2O_3 100, As_2S_3 100, As_2O_3 100)

The analytical results of the series of
experiments are given in Table I.

Double Salts of *o*-Toluidine Hydrochloride and Potassium to[illegible]

1) *Concord*

$$C_6H_5CH_2NH_2 \cdot H_2O$$
$$C_2H_4, C_2H_2 \quad \frac{7}{59\frac{1}{2}} \quad \text{✓}$$

Therap.	86	5
	16,30	89,02
	10,19	08,88
	68,58	01,87
		08,00
		08,70
		22,61
		08,77

06	2
14.06	17.06
13.89	16.71
	16.78
	16.79
	16.80
	16.81
	16.82
	16.83

Experiments with m-Toluidine Hydrochloride and
Antimony Trichloride

Mixtures of the above ingredients were made up in the usual way and well-defined crystals began to appear in each beaker as soon as the solutions were cool.

On examination of the various sets of crystals by means of the lens, they all appeared to be of the same general character. After removal from the solutions and drying, the crystals were in the form of glistening brick-red prisms.

Chemical analysis pointed in the case of each of the deposits to the formation of only one chemical compound. This proved to be tri-m-Toluidine di-iodo compound, having the formula $(C_7H_7NO)_2I_2$.

This substance, like the corresponding tri-tol compound, seems to behave in a very

Crystallizing force. A statement of the analytical results leading to the above formula will be found in the following tables.

Table II

Double salts of antimony trisulphide and antimony pentasulphide

	I	II	III	IV	V	VI	VII
	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot 2\text{H}_2\text{O}$	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$	$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$
56	19.30	19.40	19.12		19.35		
57	57.07	57.37	57.00	57.03	57.00		
58	56.77	56.75	56.86		56.75		
59	57.00	57.15	57.05	57.02	57.00		

SUMMARY II

$(\text{C}_2\text{H}_5)_2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$

Found	56	57	58	59
	19.40	19.35	19.35	19.35
	57.00	57.00	57.00	57.00
	56.93	56.93	56.93	56.93
	56.77	56.77	56.77	56.77
	57.00	57.00	57.00	57.00
	56.85	56.85	56.85	56.85

13

Experiments with potassium hydroxide and
potassium tartrate.

In working with this series some difficulty was met with in obtaining well-characterized and uniform crystals in the same beaker. From nearly every mixture worked with these crystallized out side by side light orange-colored flat prismatic crystals and darker orange-colored needles.

The prismatic forms seemed to be the more soluble of the two and by regulating the concentration of the solution it was possible to obtain a uniform crop of the needle variety. Specimens of the light prismatic type were gotten out, but on being transferred to a porous earthenware plate, began to turn orange-red immediately. Analyses of both kinds of crystals after being dried in the air, showed that there was

no difference in their composition.

The composition and name of this compound are respectively;

$\text{C}_{14}\text{H}_{10}\text{O}_4$, M_1 , A.C. BbP_3 and Mono-p-toluenic
Acid-Ortho-nitrobenzoic

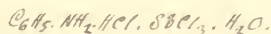
The analytical results of this series are contained in the following table

LIST OF SUBSTANCES DESCRIBED

Chlorides.

Salts of Aniline Hydrochloride and Antimony Trichloride

Mon-aniline-chlor-antimonite,

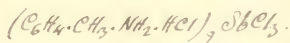


Tri-aniline-chlor-antimonite



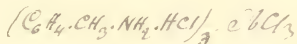
Salts of o-Toluidine Hydrochloride and Antimony Trichloride

Di-o-toluidine-chlor-antimonite



Salts of m-Toluidine Hydrochloride and Antimony Trichloride

Tri-m-toluidine-chlor-antimonite



Di-m-toluidine-chlor-antimonite



Salts of p-Toluidine hydrochloride and Antimonytrichloride

Di-p-toluidine-chlor-antimonite.



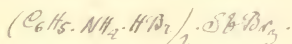
Tri-p-toluidine-chlor-antimonite.



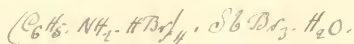
Bromides.

Salts of Aniline hydrobromide and Antimonytribromide

Di-aniline-brom-antimonite.

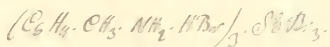


Tetr. aniline-brom-antimonite.



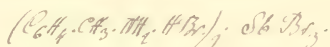
Salts of o-Toluidine hydrobromide and Antimonytribromide

Tri-o-toluidine-brom-antimonite.



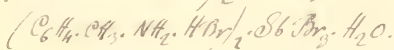
Salts of m-Toluidine hydrobromide and Antimonytribromide

Di-m-toluidine-brom-antimonite.

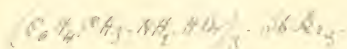


Salts of p-Toluidine hydrobromide and Antimonytribromide

Di-p-toluidine-brom-antimonite.



Tri-p-toluidine-brom-antimonite.



Tetra-p-toluidine-brom-antimonite.



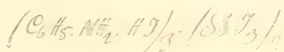
Iodides

Salts of Aniline hydroiodide and Antimonytribromide

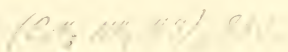
Mon-aniline-iod-antimonite.



Tri-aniline-di-iod-antimonite.

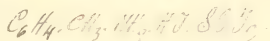


Tetra aniline-iod-antimonite.

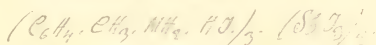


Salts of m-Toluidine Hydroiodide and Antimonytriodide.

Mono-o-toluidine-iod-antimonite.

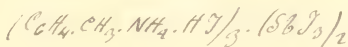


Tri-o-toluidine-di-iod-antimonite.



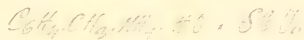
Salts of m-Toluidine Hydroiodide and Antimonytriodide.

Tri-m-toluidine-di-iod-antimonite.



Salts of p-Toluidine Hydroiodide and Antimonytriodide.

Mono-p-toluidine-iod-antimonite.



CONCLUSIONS

All of the substances above described are found to come within the scope of the law regarding the composition of double-halides, proposed by Professor Condon.

The formation of the three substances, viz., those containing four molecules of the halide of the base to six molecules of the halide of the metal, which do not appear to conform to this law has already been discussed in the Introduction.

BIOGRAPHICAL.

Howard N. Higbee, the author of this narration, was born at Lorain, Ohio on the 13th of August 1861.

His early education was obtained in the schools of Cleveland, Ohio. He entered Yale College in 1880 and graduated from there with the Bachelor's degree in 1884.

Four years were afterwards spent by him as instructor in general studies in Secondary Schools.

In 1888 he entered the Johns Hopkins University as a student of Chemistry with which he has since been connected with the exception of an interval of two years which were spent in chemical work and study in New York and in Munich.







